A PHYSICO-CHEMICAL MODEL OF THE COMETARY NUCLEUS

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A quantitative analysis of the physico-chemical surface
phenomena, likely to liberate gases from the cometary
nucleus, is attempted by deriving an equation for the total
energy balance, based on variations in entropy and enthalpy
of the changes of state. The variation in latent heat of
evaporation with the temperature is taken into considera-
tion, in determining the CH_4 and NH_3 hydrates and the ex-
cess of free methane assumed to exist in the nucleus and
coma of comets. The energy balance equation permits calcu-
lating the amount of liberated gases, the relative abundance
of the constituents of the cometary nucleus, and the surface
temperature as a function of the solar distance. On the
basis of sublimation, vaporization, and latent heat computa-
tions, it is assumed that the cometary coma consists of
porous snows of pure methane rather than of water ice.

SUMMARY

To correlate the model of cometary nuclei to the constitution of the coma,

the author attempts a quantitative analysis of the surface physico-chemical

phenomena able to liberate gases from the cometary nucleus, by covering the

variations in entropy and enthalpy of their changes of state in an equation

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* Numbers in the margin indicate pagination in the original foreign text.

giving the total energy balance. The main interest of this equation lies in that it is easy to calculate numerically for almost any model, in view of the fact that numerous Tables are in existence on the changes in entropy and enthalpy over a wide temperature range, for most of the common molecules. On the other hand, the equation also takes into consideration any variation in latent heat with temperature. This effect is by no means negligible; for example, the latent heat of CH_4 varies from 2600 cal/mole at 100° K to 2100 at 150° K, and drops to 160 only at 190° K. The results are then applied to models obtained by stipulating the simplest possible hypothesis as to the constitution of the nucleus, taking the cosmic data into consideration. Starting from the cosmic abundances, we will specifically indicate the mechanism by which the nucleus is deprived of free methane, so that the major constituents, after a certain time, will only be methane and ammonia hydrates (85%) surrounding the meteoritic fragments (15%). In this case, the equation for the energy balance makes it possible to calculate the quantity of liberated gas, the relative abundance of the constituents, and the surface temperature of the nucleus, as a function of the solar distance. This temperature, in turn, permits confirming the nature of the physico-chemical equilibria and the chemical equilibria, which had /2 been adopted in describing the surface phenomena. The calculated models predict the concentration of the parent molecule gases emitted in the coma as a function of the solar distance. The sublimation gases that feed the coma, retain almost the same composition over the entire length of the comet trajectory, a composition which is approximately defined by the existence of hydrate for methane and by the cosmic abundance of nitrogen for ammonia. The outer radius of the coma, defined by the parent molecules, as well as the radius of the "chemical" coma (where the chemical reactions almost reach equilibrium) are

calculated as a function of the heliocentric distance. In particular, it is obvious that the coma abruptly leaves the nucleus at a definite distance, ranging between 3 and 5 a.u., depending on the value of the albedo. Since the coma is mainly composed of water vapor, plus small amounts of CH_4 and NH_3, its upper layers strongly absorb solar light, specifically in the ultraviolet region, and thus heat up rapidly. Although it is obvious that the final picture of the coma must be obtained by careful considerations of the individual collisions within the middle and outer regions of the coma, the general trend is roughly indicated by the thermodynamic equilibrium. This equilibrium shows that a sufficient heating will lead to dehydrogenation reactions, yielding – in first approximation – sufficient quantities of CO, CO_2, N_2, HCN, and higher hydrocarbons to explain all the usual radicals observed in the heads and tails. This confirms that the extremely simple model adopted here is no doubt sufficient and that there is no need to conjecture on the presence, within the nucleus, of substances other than H_2O, CH_4, and NH_3 (besides the meteoritic dust).

I. THEORY OF THE PRODUCTION OF GAS BY THE COMETARY NUCLEUS   /3

The main idea of Whipple's concept (1950) on the composition of comets is obviously that the gases, present in the state of ice, in the cometary nuclei constitute an important if not predominant fraction of the mass of "new" or undissociated comets. However, although Whipple attempted to prove mathematically that the thermal insulation of the ice nucleus could explain the perihelion passages, he only qualitatively suggested that a gas loss by evaporation might explain the mass losses, estimated from the modifications observed in cometary trajectories.

We have in mind here to present a quantitative analysis of the surface

physico-chemical phenomena that might lead to liberation of certain gases from the cometary nucleus. The obtained results will then be applied to simplified physico-chemical models and compared with actual observations. Obviously, the production of gas is controlled by the surface temperature of the nucleus, since - in the final analysis - all surface chemical or physico-chemical processes depend on this temperature, specifically the vaporizations proper but also the possible phenomena of desorption, chemisorption, change of phase (solid - liquid), or even chemical reactions. Therefore, before going further, it is useful to give a brief survey over the data reported to date with respect to the surface temperature of the cometary nucleus. The situation can be summarized by stating that the models studied until now were not sufficiently general for covering the entire complex of all possible phenomena. For example, Minnaert (1947) obtained temperature curves as a function of the heliocentric distance r, by integrating the equation of heat conduction. Although his model is quite excellent for describing the metal or stone meteoritic nucleus, it is not applicable to the vaporization of ice, a point that had not been seriously considered at his time. Levin (1948), who suggested a mechanism of desorption for feeding the gases of the coma, first used a simple model   /4 and was satisfied with writing the surface temperature in the classical form of $T = T_0 r^{-\frac{1}{2}}$ [eq.(1)], obtained from the equilibrium between the incident solar energy flux and the radiation given by Stefan's law, which indicates that the heat of desorption is negligible with respect to the energies involved. Later, Delsemme and Swings (1952) introduced the rate of evaporation , calculated on the basis of the kinetic theory of gases and of saturated vapor pressures, but did not use these data for calculating the temperature. Dobrovolsky (1953), basing his calculations independently on the same principles, calculated an

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approximate value for the temperature (see Note 1)[*] which had been used by
Markovich (1958) for writing $T = T_0 r^{-\alpha}$ where α has a value ranging between 0.11
and 0.16 depending on the vaporizing substance, being 0.16 for water and 0.11
for methane.

Markovich (1959) calculated the temperature of nuclei of pure water, of
pure CH_4, and of a mixture of 50% CH_4 with 50% of meteoritic substances, as a
function of the time along the theoretical orbits. Squires and Beard (1961)
also calculated the temperature of two schematic models (nucleus in the form of
a disk; zero albedo), one for pure water and the other for one third water and
two thirds of a mean molecule close to NH_3, with the object of studying the
orbital perturbations produced by the evaporation. Watson, Murray, and Brown
(1963), using a modified model, calculated the temperature of water-ice spheres,
during a study on the stability of volatile substances present in the solar
system. None of these investigations allows for variations in the latent heat
with the temperature, despite the fact that this variation frequently exceeds a
factor of 2 and occasionally a factor of 10. For example, in calculating the
latent heat of methane, by the variation in free energy of the change of state
at different temperatures, it will be found that this heat passes from a value
of 2600 cal/mole at $100^{\circ} K$ to 2100 cal/mole at $150^{\circ} K$ and even drops as low as
160 cal/mole at $190^{\circ} K$ because of the approach to the critical point. Therefore,
it is suggested to use any mean value with great caution and to apply it only
if there is no other way, since a part of the physical significance of the ob-
tained results could easily be lost. Particularly, the Markovich formula $T =$ /5
$= T_0 r^{-\alpha}$ seems too schematic for our purpose. The quantity α cannot be taken as
constant for a given substance since it varies strongly as a function of the

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[*] Notes are assembled at the end of the text.

heliocentric distance.

1. Equation of the Steady State

To express the surface thermal equilibrium in the steady state, it will be sufficient to stipulate that, at any point of the surface of the nucleus, the radiation E absorbed per unit surface is equal to the radiation E_r from the nucleus into space plus the liberation of free energy E_g due to the surface physico-chemical process (phase changes, chemical reactions between molecules or radicals, liquid or solid solutions, desorptions or chemisorptions, etc.) and plus the energy dissipated toward the interior of the nucleus E_i :

$$E_a = E_r + E_g + E_i \tag{1}$$

Whipple (1960) showed in a convincing manner that the transfer of heat by radiation governs the thermal exchanges at the center of the nucleus, while both convection and conduction are negligible there. He also demonstrated that this mode of heat transfer is several orders of magnitude smaller than the surface phenomena to be studied here, so that his results make it possible for us to neglect the transfer of heat through the nucleus in the calculation of the surface thermal equilibrium. Markovich (1958) studied the influence of the flow of gases due to evaporation through the surface layer of the cometary nucleus and finally came to the same conclusions, in view of the fact that a molecular flow is involved here, which is always the case for the production of gases discussed below and for surface pores smaller than one centimeter. In what follows, we can thus use $E_i = 0$ once and for all.

On the other hand, E_g is expressed by the change in free energy per molecule ΔG_i , multiplied by the number P_i of initial molecules that undergo phase

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changes or that are chemically converted, per cm^2 and per sec. The change in free energy ΔG_i, produced by the change in phase, or the chemical reaction of <u>/6</u> the constituent i, at the temperature T, can then be written as

$$\Delta G_i = \Delta H_i - T\Delta S_i \tag{2}$$

Here, H_i and S_i are, respectively, the variations in enthalpy and entropy per molecule, referred to the change of state or to the chemical reaction of the constituent i. If we first limit our calculation to physico-chemical changes of state (for example, sublimation of ice), the number of molecules undergoing changes of state per second at the surface of the nucleus will be equal to the number of molecules of gas striking the interface between the phases, such as can be calculated on the basis of the kinetic theory of gases (see Note 2). Denoting by n_i the number of molecules per cm^3 and by m_i the molecular mass of the species i in the saturated vapor at a pressure p_i and a temperature T and, on the other hand, denoting by $\overline{c}_i$ their mean-square velocity, we will obtain

$$P_i = \frac{1}{3} n_i m_i \overline{c}_i^2 = n_i kT$$

This readily shows that the gas production P_i, expressed in gm/cm^2, is equal to

$$P_i = bp_i \left(\frac{m}{kT} \right)^{\frac{1}{2}} \tag{3}$$

where b is a purely numerical coefficient (see Note 3). Then p_i can be expressed, in turn, as a function of the variation in free energy of the change of state, by

$$\text{Log } p_i = - \frac{\Delta G_i}{RT} = \frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT} \tag{4}$$

After this, eq.(1) can be written in explicit form; E_a is given by the relation

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in r^{-2}, applied to the solar energy flux illuminating a surface inclined at an angle θ, while E_r is given by Stefan's law and E_s by eqs.(2) and (4).

From this, we obtain

$$F_0(1 - A_0)\, r^{-2}\, \cos\theta = \sigma(1 - A_1)T^4 + b(kT)^{-1/2} \sum_i (\Delta H_i -$$

$$- T\Delta S_i)\, a_i\, m_i^{1/2}\, \exp\left(\frac{T\Delta S_i - \Delta H_i}{RT}\right) \tag{5}$$

where F_0 is the solar flux at the terrestrial distance; A_0 is the albedo of the cometary nucleus for solar radiation; r is the distance from the sun in astronomical units; θ is the angle made by the normal to the surface with the direction to the sun; σ is Stefan's constant; A_1 is the albedo of the cometary nucleus for the temperature radiation T; while T is the temperature of sublimation of the surface ice; k is the Boltzmann constant; and a_i is the fraction of the constituent i which participates in the surface evaporation.

Equation (5) defines T at any point of the illuminated surface of the cometary nucleus, as a function of the solar distance, for the case that the rotation of the nucleus as well as the fluctuations of F_0 are slow with respect to establishing the thermal equilibrium. If, conversely, the rotation is sufficiently rapid to produce temperature equilibrium, the quantity $\cos\theta$ can be replaced by 1/4 in eq.(5), using conventional arguments.

This equation is useful in combination with existing Tables of ΔS and ΔH which were established, as a function of the temperature, for most changes of state or ordinary molecular reactions. A further simplification of this particular equation for the case of substances for which no ΔS and ΔH Tables exist and for the case of only simple changes of state, is the following: In the temperature range in question, for example from $50°$ to $500°$ K, the variations in entropy

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and enthalpy, associated with the change of state of a certain number of ordinary molecules, are negligible, as proved by the vapor-tension curves of which large segments can be fitted to straight lines, in the diagram log p versus 1/T. This permits using the Clapeyron approximation, if desired. On the other hand, it may frequently occur that a single constituent predominates in the vaporization mechanism, in which case the summation sign vanishes; then the doubly simplified equation will assume the following form:

$$F_0(1 - A_0)r^{-2} \cos \theta = \sigma(1 - A_1)T^4 + \left(\frac{m}{3kT}\right)^{1/2} L \exp \ B - \left(\frac{L}{RT}\right) \tag{6}$$

where L is the mean heat of vaporization of the major constituent while B = $\underline{/8}$ = $\frac{\Delta S}{R}$ is a constant that can be determined from a single saturated vapor pressure. This equation defines the surface temperature at various points of the illuminated hemisphere, as a function of the solar distance, of the vapor pressure, and of the mean latent heat of vaporization of the major constituent.

To apply eqs.(5) or (6), it is now necessary to select a definite model of the cometary nucleus. This means a choice of hypotheses which should be reduced to a minimum and should be clearly defined.

II. CONCRETE MODEL OF THE COMETARY NUCLEUS

As basic hypothesis, it is accepted here that the elements were present at the ratio of cosmic abundance during the process (no matter of what type) that led to condensation of the cometary mass; in addition, it is assumed that, at the beginning, a large superabundance of hydrogen existed which hydrogenized any hydrogenizable material within reach before disappearing more or less rapidly together with the lightest rare gases, either by evaporation or simply by never condensing.

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Assuming, at this stage, that the free radicals have been able to exist for a certain time, an important argument by Urey (1952) must be recalled, who mentioned that free radicals such as C, CH, CH_2, CH_3, N, NH, NH_2, O, and OH must be strongly absorbed by solid surfaces because of their unsaturated bonds and that, consequently, the slightest amount of dust would energetically catalyze their recombination with the hydrogen present. Although this mechanism is not necessarily highly efficacious in points of space where the mean free paths are enormously long, it does have some value for a cometary nucleus under formation. It is true that Donn's arguments (1955) lead one to believe that certain specific mechanisms, of which one extreme case may go as far as poisoning the catalysis by well-selected impurities, can be used for preserving certain free radicals in the cold over a certain length of time. Nevertheless, the general rule remains valid that chemical equilibria have a tendency to become established, specifically during the extremely long times in question in astronomy. If free radicals actually do exist, it is not impossible that they might play /9 an important role in the explanation of certain limited phenomena; however, these radicals must of necessity represent a negligible mass relative to the mass of stable molecules. Without denying the importance of laboratory studies on the behavior of free radicals at low temperatures, to increase present knowledge in a field in which our ignorance is still great, we will nevertheless assume below (in lieu of anything better) that chemical equilibria were in fact established and that the consequent hydrogenation had rapidly resulted in the appearance of large amounts of stable molecules of H_2O, CH_4, and NH_3. It should be mentioned that, since the presence of CH_4 is incompatible with the existence of CO_2, it is easier to explain the phenomena of dehydrogenation than the inverse situation. The only uncertainty remaining concerns the fact that, if free

radicals had temporarily existed, they could immediately have produced complex molecules whose simplest types would have been, for example, C_2H_6, N_2H_4, C_3H_8, and HCN. This might also have been causative for unsaturated hydrocarbons such as C_2H_2 or C_2H_4 which, although in a metastable chemical state relative to H_2, would be able to subsist for long periods of time at low temperatures, much more so than the free radicals, and would thus constitute an appreciable chemical potential for explaining subsequent mechanisms, as had actually been done earlier by the author (Delsemme, 1953).

To give a general idea, we will consider below a mass of 10^{18} gm of matter, distributed over a sphere having a radius of the order of 10 km (see Note 4). Assuming the usual cosmic abundance ratios for O, C, and N (see Note 5), the model of a cometary nucleus would have to contain, in principle, the following constituents:

$$60 \times 10^{16} \text{ gm} = 20 \times 10^{39} \text{ molecules of } H_2O$$

$$20 \times 10^{16} \text{ gm} = 7 \times 10^{39} \text{ molecules of } CH_4$$

$$6 \times 10^{16} \text{ gm} = 2 \times 10^{39} \text{ molecules of } NH_3$$

$$14 \times 10^{16} \text{ gm} = 1 \times 10^{39} \text{ molecules (Fe, Mg, Si, S etc.).}$$

However, as soon as the temperature is not too high, for example less /10 than $150°$K (see Note 6), NH_4 and CH_3 are bound to react with the water to form hydrates (Delsemme and Swings, 1952); NH_3 will have formed the ionic hydrate, NH_4OH, while CH_4 will have formed the nonionic hydrate of the clathrate type, which – for simplification – we will assume to be very close, at low temperatures, to the formula $CH_4 \cdot 6H_2O$ (see Note 7). The first compound to form is NH_4OH since the variation in free energy, produced by the hydration of NH_3, is much greater than that of the conversion of CH_4 into a hydrate; in fact, the model contains the constituents compiled in Table I.

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TABLE I

MODEL WITH NONHYDRATED EXCESS METHANE (See Note 8)		
CH_4 excess	12×10^{16} gm = 4×10^{39}	molecules of CH_4
CH_4 hydrate	62×10^{16} gm = 3×10^{39}	molecules of $CH_4 \cdot 6H_2O$
NH_3 hydrate	12×10^{16} gm = 2×10^{39}	molecules of NH_4OH
Meteoritic particles	14×10^{16} gm = 1×10^{39}	molecules

Obviously, only an indicative value is to be attached to these numerical evaluations. Our preliminary discussion mainly is to demonstrate that a sufficiently large excess of nonhydrated CH_4 is by no means impossible and is even quite probable. Considering that the methane is by far the most volatile of the still present molecules, the fact that this CH_4 excess has not been evaporated since long can be attributed to the finding that the nucleus has remained extremely cold, at a temperature not more than a few tens of $^{\circ}K$, which is not incompatible with present concepts (Oort, 1950) on the origin of comets. However, Whipple (1950) has convincingly demonstrated that the center of the cometary nucleus is extremely well insulated and that practically no heating takes /11 place there during its passage through perihelion.

This raises the question as to whether the matter might be stratified into differentiated loops in accordance with their depth in the nucleus. It is true that gravity is weak here, but it is not absolutely zero (being of the order of 10^{-4} g). The coarsest particles of the meteoritic matter (representing about 15% of the total mass) no doubt have produced a certain sedimentation toward the center of the nucleus, whereas the finest dusts may possibly have remained in suspension within the exterior snows. These dusts represent at most 10% of the surface substance. So far as the ice or snow are concerned, the situation must

TABLE II /12

DENSITY OF HYDRATES (1)

	T_{fusion}	$d_{(liquid)}$	$d_{(solid)}$	
Water	$273°$ K	1.000	0.915	
CH_4 hydrate	(2)	(2)	0.896	
Crystallized water according to the hydrate lattice, but stripped of CH_4	(6)	(2)	0.798	
NH_3 hydrates:				
Eutectic $NH_3 \cdot 1.8\ H_2O$	$184°$ K	0.880 (3)	0.92	(4)
Eutectic $NH_3 \cdot 0.74\ H_2O$	$189°$ K	0.812 (3)	0.86	(4)
Eutectic $NH_3 \cdot 0.24\ H_2O$	$187°$ K	0.711 (3)	0.80	(4)
NH_3	$195°$ K	0.618 (3)	0.817	
CH_4	$90°$ K	0.415 0.16 (5)	0.44	

(1) Densities for temperatures close to the fusion point, except if specified differently (Perry, 1950).

(2) Does not exist

(3) At $300°$ K

(4) Extrapolated

(5) At $190°$ K

(6) Unknown.

be studied with extreme care (see Table II). Ice of water or of hydrates always has a density between 0.80 and 0.92. Conversely, ice of nonhydrated CH_4 has a density of the order of 0.44, so that it is not difficult to imagine a sedimentation mechanism which would have entrained the largest hydrate crystals toward the center and would have left the CH_4 at the surface. A separation of the hydrates of CH_4 from those of NH_3 is more difficult. It is certain that the size of the individual crystals constitutes the decisive factor for this separation within the snow in question. If the crystals are coarse - which is probable since they had an opportunity to grow very slowly - sedimentation will be facilitated. Without taking a definite stand, we will assume, for the above-considered model, that a surface layer of pure methane snow is present.

1. Model with Methane Excess

During the first passage through perihelion, a large amount of nonhydrated methane will sublime in the surface layer. No matter whether other substances were or were not present in this layer, the sublimation of methane is the only effective mechanism whenever the surface temperature is below $90^\circ K$. At $90^\circ K$, convection mechanisms in liquid phase could have appeared at the instant of fusion of the methane, but we will demonstrate that this is never the case (see Note 9).

It is now possible to apply eq.(5) to the case of nonhydrated methane. Table III gives several numerical results, calculated directly from eq.(5) by setting $A_0 = 0.1$ (see Note 8). The main characteristic of these results - a point to be specifically emphasized - is that cooling of the nucleus surface by sublimation of the ice is particularly intense since the surface temperature, at the subsolar point, reaches only $70^\circ K$ at 0.1 a.u. Once this temperature is

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determined, a calculation of the NH₃ production will become possible provided that NH₄OH had been present in the surface layer. This production, as indicated in Table III, is much too weak for disturbing the temperature calculated exclusively for CH₄.

TABLE III

COMET WITH NONHYDRATED METHANE EXCESS.
SUBLIMATION OF THE METHANE EXCESS

r in a.u.	T At the Sub-solar Point (see Note 11)	Production of Gaseous CH₄ gm/sec	Production of Gaseous NH₃ gm/sec	Density of the Gases Near the Nucleus cm^{-3}	Mean Free Path Near the Nucleus cm
4.8	50° K	2×10^7	10^2	2.4×10^{14}	0.76
1.5	55° K	2×10^8	10^3	2.2×10^{15}	0.08
0.49	60° K	2×10^9	10^4	2.0×10^{16}	0.01
0.09	70° K	8×10^{10}	4×10^5	1.0×10^{18}	2×10^{-4}

The production of gaseous CH₄, shown in Column 3 of the Table, as well as /14 that of NH₃ given in Column 4, were obtained by integration over the illuminated hemisphere of the nucleus. Column 5 describes the density of the gas close to the nucleus, which consists almost exclusively of methane. The last column gives the mean free paths in the coma near the nucleus.

We then summarily integrated the production of gaseous CH₄ along three parabolic trajectories, having perihelion distances of 4.8, 1.5, and 0.5 a.u. Table IV gives the number of perihelion passages of this type, likely to cause the total loss of nonhydrated methane, always provided that this is possible at all.

The conclusion is obvious: The comets having an excess of nonhydrated

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methane, if they exist at all, must have special characteristics which are lost on their first passage through the perihelion.

TABLE IV

TOTAL LOSS OF NONHYDRATED METHANE

Perihelion Distance	Number of Necessary Perihelion Passages
4.8 a.u.	4.0
1.5 a.u.	2.6
0.5 a.u.	0.5

The model with an excess of methane thus describes a "new" comet whose surface temperature would always remain extremely low and vary little. The coma of this comet would be exclusively composed of methane and, consequently, could be detected only by its possible entrainment of meteoric dusts. It might well be that our model can be correlated with the fact that "new" comets mainly show the diffused solar spectrum while "old" comets show highly developed gas spectra (Oort and Schmidt, 1951). To check whether this interpretation can be numerically defended, we will consider the case of the Arend-Roland comet of /15 which homogeneous photometric observations are in existence (Beyer, 1959). Using this photometry in applying the concepts of Dobrovolsky (1953) and of Markovich (1958 and 1959), Sekanina (1962) calculated a mean latent heat of evaporation of $L = 5400 \pm 160$ cal/mole, assuming a surface temperature of the nucleus of $T_0 = 160^\circ$ K at 1 a.u. and an exponent of $\beta = 14.3$ in the formula for the saturated vapor pressure of the gas during evaporation $p = AT^\beta$. There is a difficulty inherent to these results, since the only gas which, according to this author, has a value of β close to 14.3 is CH_4 ($\beta = 13.1$), which has a

latent heat of evaporation close to 2000 cal/mole at a temperature of 160° K, i.e., almost three times less than the heat determined by him.

If the calculations of this author were repeated with the excess methane model, it would be found that the photometric curve of the Arend-Roland comet must be associated with a temperature of $T_0 = 57^{\circ}$ K at 1 a.u., which would yield a mean latent heat of L = 2000 cal/mole, a value which agrees much better with pure CH_4 than with any other substance. In particular, water seems completely excluded from the vaporization process observed in the Arend-Toland comet (see Table V).

TABLE V

COMPARISON OF THE HEATS OF VAPORIZATION

	H_2O	CH_4	Arend-Roland Comet
L cal/mole, corresponding to T_0	6800	2600	2000[*]

* The photometric curve used here corresponds to a heliocentric distance ranging from 0.5 to 4 a.u.

Because of the observation errors, the great simplification introduced, and the fact that a mean value was assumed for L, no better coincidence than a constant for β can be expected here (see Note 1).

This seems to indicate that the Arend-Roland comet is a typical example for a comet having a surface layer of methane snow, covering other hydrate snows.

2. Model without Methane Excess

We would like to investigate now what happens when an "old" comet, or a

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comet that never had possessed an excess of nonhydrated methane, approaches the sun.

The low density of the methane snow particles previously induced researchers to use a model in which the surface layer could be pure methane.

TABLE VI

MODEL WITHOUT METHANE EXCESS

CH₄ hydrate	62×10^{16} gm $= 3 \times 19^{39}$ molecules of $CH_4 \cdot 6\ H_2O$
NH₃ hydrate	12×10^{16} gm $= 2 \times 10^{39}$ molecules of NH_4OH
Meteoritic particles	14×10^{16} gm $= 1 \times 10^{39}$ molecules Fe, Si, etc.)

Conversely, the greater densities and the rather close values of these densities of the snow particles, formed by the hydrates and the water ice, seem to indicate that a homogeneous structure might be in question for the present model. In this case, a quasi-steady state might be rapidly attained, so far as the ratio of the evaporation rates is concerned (see Note 12). For this, the /17 mechanism of establishing equilibrium must first be described, a mechanism which had already been briefly mentioned by Whipple (1950).

The substance A, which evaporates most, establishes the surface temperature T_A by its rate of evaporation. However, because of its evaporation, the surface concentration of this substance decreases progressively. Thus, in depth, a concentration gradient of A is formed along the temperature gradient; the result is the same as if this substance had disappeared up to a certain colder isotherm $T_A' < T_A$, while remaining at its former concentration at greater depths.

Similarly, the pressure increases slowly the more one penetrates into the

surface; at each depth, dynamic equilibrium exists between the hydrate crystals more or less loaded with CH_4 and NH_3 and the gaseous CH_4 and NH_3, at a pressure that increases continuously although it does remain below the dissociation pressure at the temperature of the depth under consideration, since the dissociation stops exactly as soon as this pressure is reached. The variation in pressure with depth is defined by the pressure drop produced by the molecular flow of vaporized gases through the capillaries leading to the surface. For balancing the dissociation pressures considered here, a pressure of only a few microns of mercury is required; it is known in laboratory practice that the length of tubing required for producing such a pressure drop is not excessive (see Note 13).

However, everything passes as though the phenomenon were limited to the isotherm T_A'. The temperature T_A' would define the new rate of evaporation of the substance, with the remainder being furnished by an increase in evaporation rate of the substance B, which exhibits surface heating up to a temperature T_B.

At equilibrium, since we assume here that the phenomena are stationary, the isotherm T_A' will stop at a depth for which the evaporation rates are at a mutual ratio of relative concentrations, where the depth depends exclusively on the conductivity of the surface layers. This conductivity, however, will not be the conductivity by pure radiation as considered by Whipple for deeper layers. Rather, the conductivity here is modified by the heat transfer produced by /18 the (weak) gaseous flux of the evaporations. On the surface, a molecular flow is involved since the mean free paths of the evaporated molecules are of the order of 1 m near 3 a.u. and of the order of 1 dm near 1 a.u., while they are of the order of 1 cm near 0.5 a.u. (see Table VIII); the surface snow is visualized as being composed of fine crystals interlinked by ice needles whose pores

are no doubt of the order of 1 mm. The two major constituents, at present, are CH_4 hydrate and then NH_3 until finally the composition is exclusively water snow. The isotherm where the NH_3 hydrate is undergoing dissociation will stabilize, after a certain time, at a definite depth; in the same manner, the isotherm where the CH_4 hydrate undergoes dissociation will stabilize, again after a certain time, at a greater depth. The depth of the various isotherms depends mainly on the calorific conductivity and thus cannot be better defined. The analysis by Whipple (1950) permits only the statement that these depths are minor. Conversely, the temperatures and production of gaseous molecules can be recalculated by means of eq.(5), taking into consideration the fact that, as soon as the steady state is reached, the supplementary condition that the productions are proportional to the concentrations will be satisfied.

Since no ΔS and ΔH Tables exist for the CH_4 hydrate, we used the approximation (6) of the equation of the energy balance; the experimental values on vapor tensions (see Notes 14 and 15), obtained by Miller (1961) were used for calculating the mean value of the heat of dissociation of the hydrate.

An integration of the production on the illuminated surface of the nucleus results in Table VII which is compiled for a series of solar distances ranging from 7 a.u. to 0.015 a.u. For convenience of calculation, T_0 was adopted as an independent variable, and the Tables were calculated from 10^0 to 10^0. Here, T_N and T_c were calculated a posteriori, in accordance with the production of NH_3 and CH_4 determined by the steady state. It is of interest to note that the surface temperature is determined exclusively by Stefan's law for distances greater than 6 a.u. and exclusively by rates of evaporation at distances smaller than 0.5 a.u.; the distances from 6 to 0.5 a.u. are exactly the most interesting since they constitute a transition region where the two terms exchange their /19

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order of magnitude.

TABLE VII

COMET WITHOUT METHANE EXCESS
SUBLIMATION OF CH_4 AND NH_3 HYDRATES

r a.u.	T_0 °K	Production of Gaseous H_2O gm/sec	T_N	Production of Gaseous NH_3 gm/sec	T_c °K	Production of Gaseous CH_4 gm/sec
6.93	150°	5.1×10^3	72°	4.8×10^2	48°	6.9×10^2
6.18	160°	5.7×10^4	82°	5.4×10^3	55°	7.6×10^3
5.10	170°	4.8×10^5	91°	4.5×10^4	62°	6.5×10^4
3.70	180°	3.7×10^6	101°	3.5×10^5	69°	5.0×10^5
2.18	190°	1.8×10^7	110°	1.7×10^6	76°	2.4×10^6
1.13	200°	9.0×10^7	120°	8.5×10^6	82°	1.2×10^7
0.605	210°	3.5×10^8	130°	3.3×10^7	87°	4.7×10^7
0.305	220°	1.4×10^9	139°	1.3×10^8	92°	1.9×10^8
0.179	230°	4.1×10^9	146°	3.9×10^8	97°	5.5×10^8
0.114	240°	1.0×10^{10}	152°	9.5×10^8	102°	1.3×10^9
0.066	250°	3.2×10^{10}	160°	3.0×10^9	107°	4.3×10^9
0.041	260°	8.0×10^{10}	165°	7.5×10^9	112°	1.1×10^{10}
0.026	270°	1.9×10^{11}	171°	1.8×10^{10}	117°	2.5×10^{10}
0.021	280°	3.8×10^{11}	175°	3.6×10^{10}	121°	5.1×10^{10}
0.015	290°	6.8×10^{11}	179°	6.4×10^{10}	124°	9.1×10^{10}

T_0 surface temperature, at the subsolar point, of the water snow during sublimation.

T_N temperature, below the subsolar point, at the depth of the isotherm where the NH_3 hydrate undergoes dissociation.

T_c temperature, below the subsolar point, at the depth of the isotherm where the CH_4 hydrate undergoes dissociation.

It should be mentioned here that the water snow on the surface will [20] liquify only at the very short distance of 0.025 a.u. from the sun and that the ammonia hydrate isotherm reaches the fusion points of the eutectics (189° K, 167° K, 184° K) only at a still shorter distance (see Note 16) of 0.014 a.u. from the sun, whereas the CH_4 hydrate can never reach this point.

The hypothesis that the water snows and the hydrate snows remain dry snows

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after several passages through the perihelion is thus confirmed, except for very rare comets. This statement is specifically important with respect to the albedo of the nucleus which could decrease abruptly if the liquids would "wet" the surface snows.

Because of the existence of a quasi-steady state in the sublimations, it is obvious that the composition of the gas emitted by the nucleus will remain approximately constant, no matter what the surface temperature (or the solar distance) might be, corresponding to

$$80\% \quad H_2O \quad 12\% \quad CH_4 \quad 8\% \quad NH_3.$$

The abundance ratio H_2O/NH_3 only reflects the cosmic abundance ratios assumed between O and N, whereas the ratio H_2O/CH_4 is fixed by the presence of methane hydrate, with the possible excess methane having escaped at a previous stage.

On the other hand, the production of gaseous molecules is given by eq.(3) in the form of a flux of particles whose mean velocity $\bar{c}_i = \left(\frac{5kT}{m} \right)^{\frac{1}{2}}$ is known and from which one can thus immediately derive the number n_i of molecules i per cm^3. In fact, under the considered conditions of molecular flow, the velocity of flow in a definite direction is given by the mean velocity of the molecules, divided by $\sqrt{3}$ (see Note 17).

It has been assumed that the CH_4 and NH_3 molecules, originating from much colder isotherms present in depth, are heated by collision to the surface temperature, on traversing the pores of the surface snow. This makes it possible to calculate the total number of molecules per cm^3 in the gaseous phase, at the surface of the nucleus. This number of molecules is given in Column 2 of Table VIII. Column 3 gives the mean free path on the nucleus surface, for H_2O and CH_4 molecules of identical molecular diameter. (The mean free path of NH_3

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is 1.18 times greater.) To give a general idea on the dimensions of the entire coma, we arbitrarily limited its radius R to the point at which the mean free path of the water molecules ℓ_R, calculated at the surface temperature, becomes equal to $\frac{R}{100}$. This is a point with a constant optical density, no matter what values ℓ_R or R might have, which permits a direct comparison with the observed dimensions.

Finally, Column 4 gives the radius of the central portion of the coma where the mean free paths are sufficiently small for allowing the chemical reactions in the gaseous phase to reach equilibrium. This has been defined as the radius for which the mean free path becomes equal to 4 m; in the terrestrial atmosphere, mean free paths of this order are reached near 140 km, which is the altitude that clearly separates the low ionosphere (D and E layers) from the high iono-sphere (F_1 and F_2 layers). This empirically justifies the arbitrary definition adopted here.

Obviously, the "chemical" coma is abruptly generated near 4.a.u. The coma extends to a height of 5 km above the surface of the nucleus at 3.70 a.u. and of 60 km at approximately 1 a.u., while the height is 250 km near 0.3 a.u. Not only are chemical reactions possible in this coma but the collisions are also sufficiently numerous to ensure an equipartition of energy, so that thermody-namical equilibrium is established.

Conversely, the "middle" coma represents a region in which thermodynamic equilibrium is less and less likely to occur the more one goes away from the nucleus; but the collisions still remain sufficiently numerous for having a certain number of bimolecular individual processes remain effective for the formation of new molecules.

However, it should be recalled that only a fictive distribution of parent

molecules is involved here, in the absence of any heating, excitation, dissociation, or ionization produced by the light or by solar particles.

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TABLE VIII

COMET WITHOUT METHANE EXCESS
BUILD-UP OF THE COMA BY H_2O, CH_4, AND NH_3

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r a.u.	Density Near the Nucleus n/cm^3	Mean Free Path ℓ_s cm	Mean Height of the Coma (1) H_m km	Chemical Height of the Coma (3) H_{ch} km	Optical Thickness cm H_2O vap. T.P.N.
6.93	2.56×10^9	7.1×10^4	(2)	(4)	7.1×10^{-5}
6.18	2.75×10^{10}	6.6×10^3	5	(4)	7.7×10^{-4}
5.10	2.26×10^{11}	8.0×10^2	1.1×10^2	(4)	6.3×10^{-3}
3.70	1.69×10^{12}	1.1×10^2	9.0×10^2	10	4.7×10^{-2}
2.18	8.00×10^{12}	2.3×10	4.3×10^3	32	2.1×10^{-1}
1.13	3.90×10^{13}	4.7	2.1×10^4	83	1.4
0.605	1.47×10^{14}	1.2	8.2×10^4	176	5.3
0.305	5.42×10^{14}	3.3×10^{-1}	2.9×10^5	330	1.9×10
0.179	1.64×10^{15}	1.1×10^{-1}	9.1×10^5	600	5.9×10
0.114	4.12×10^{15}	4.4×10^{-2}	2.2×10^6	940	1.5×10^2
0.066	1.24×10^{16}	1.5×10^{-2}	6.8×10^6	1640	4.5×10^2
0.041	2.95×10^{16}	6.2×10^{-3}	1.6×10^7	2550	1.0×10^2
0.026	7.01×10^{16}	2.6×10^{-3}	3.8×10^7	3900	2.6×10^3
0.021	1.39×10^{17}	1.3×10^{-3}	7.7×10^7	5500	5.0×10^3
0.015	2.37×10^{17}	7.7×10^{-4}	1.1×10^8	7400	8.0×10^3

The height H is the radius of the coma R, less the radius of the nucleus R_0.

(1) The radius R_m of the mean coma is arbitrarily limited to the site where the mean free path of the molecules ℓ_R becomes equal to 0.01 R.

(2) The radius R_m is smaller than the nucleus; the coma does not yet exist.

(3) R_{ch} is defined as the radius of the volume within which the mean free path is less than 4 m.

(4) The radius R_{ch} is smaller than the nucleus; the "chemical" coma does not yet exist.

3. The Coma in the Solar Field

Finally, we would like to discuss a model based on the interaction of the solar ultraviolet and solar particles with the coma of parent molecules obtained by evaporation of the cometary nucleus model, studied above.

It is obvious that a final picture of the coma can be obtained only by a careful consideration of all possibilities of individual collisions between molecules, ions, and radicals formed by the excitations, ionizations, and dissociations attributable to the ultraviolet or to the solar particles. Specifically, this method is the only one that might lead to a significant result in the regions at the middle and exterior of the coma, where the dilution of the particles is sufficient for making an approach to thermodynamic equilibrium impossible, as is clearly evidenced by the fictive temperatures observed for C_2 or by the intensity ratios of the green and red lines of [O1].

However, we have just shown that also an interior region exists, known as the "chemical" coma where thermodynamic equilibrium is reached. This region is duplicated by an undefined but rather large region where the thermodynamic equilibria, although not fully established, give a good indication of the chemical reactions taking place, since the molecular collisions are still quite high there. To calculate these equilibria, one must have some idea on the temperature distribution within the coma.

To obtain such information, we will consider the overall heating of the coma by the solar light.

The last column in Table VIII expresses the optical thickness of the   /24 cometary atmosphere, given in atm/cm water. This column results from an integration of the concentrations calculated from the nucleus surface to infinity.

Table IX gives the absorption, at 1 a.u., of the ultraviolet radiation of the sun at several thicknesses of water vapor, expressed in atm/cm (optical thickness of 1 cm at normal temperature and pressure).

The interval from 700 to 1900 Å has been used here since it corresponds to the most intense absorption bands of water.

TABLE IX

ABSORPTION OF THE ULTRAVIOLET RADIATION OF THE SUN BY WATER
VAPOR, AT A DISTANCE OF 1 a.u. FROM THE SUN, IN
erg/cm^2/sec FOR EACH SPECTRUM INTERVAL CONSIDERED

	From 700 to 1000 Å	From 1000 to 1300 Å	From 1300 to 1600 Å	From 1600 to 1900 Å	Total from 700 to 1900 Å
Solar I_0	1.0	1.4	5.4	85.0	92.8
Absorption of 10 μ H_2O	−0.7	−0.1	−0.0	−0.5	−1.3
Residual I_1	0.3	1.3	5.4	84.5	91.5
Absorption of 100 μ H_2O	−0.3	−0.9	−0.3	−4.3	−5.8
Residual I_2	0	0.4	5.1	80.2	85.7
Absorption of 1 mm H_2O	−	−0.4	−2.3	−22.1	−24.8
Residual I_3	0	0	2.8	58.1	60.9

The spectral distribution of the solar ultraviolet intensities was taken /25 from recent data given by Hinteregger (1961), Hinteregger et al. (1962), Bourdeau et al. (1964), while the absorption coefficients of the water vapor are those given by Allen (1955).

From these data, it is possible (for example) to calculate the height at which a certain temperature is reached in the coma, for various distances from

the sun. Table X gives some results obtained by a simple graphic integration, based on a temperature of 1500° K at which the water molecule does not yet radiate noticeably.

TABLE X
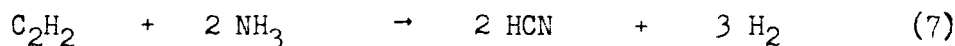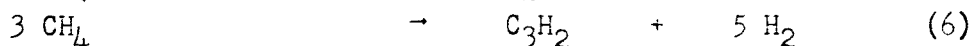
HEIGHT IN THE COMA AT WHICH A TEMPERATURE OF 1500° K IS REACHED
BY SIMPLE HEATING OF THE WATER VAPOR BY THE SOLAR ULTRAVIOLET

r in a.u.	Height of the Isotherm 1500° K	Chemical Coma	Middle Coma
3.70	5,300 km	10 km	900 km
2.18	1,700 km	32 km	4,300 km
1.13	940 km	83 km	21,000 km
0.605	240 km	176 km	82,000 km

It is obvious that the temperature of 1500° K, although it does remain outside of the chemical coma proper up to 0.6 a.u., penetrates into the middle coma near 3 a.u., with this "middle" coma being defined as the region in which the collisions are still sufficiently numerous to produce bimolecular reactions.

However, a heating of the gas composed of 80% H_2O, 12% CH_4, and 8% NH_3 /26
will lead to a progressive dehydrogenation of the constituents, in accordance with the following reactions:

$$H_2O \ + \ CH_4 \ \rightarrow \ CO \ + \ 3 \ H_2 \qquad (1)$$
$$H_2O \ + \ CO \ \rightarrow \ CO_2 \ + \ H_2 \qquad (2)$$
$$NH_3 \ + \ CH_4 \ \rightarrow \ HCN \ + \ 3 \ H_2 \qquad (3)$$
$$2 \ NH_3 \ \rightarrow \ N_2 \ + \ 3 \ H_2 \qquad (4)$$
$$2 \ CH_4 \ \rightarrow \ C_2H_2 \ + \ 3 \ H_2 \qquad (5)$$
$$3 \ CH_4 \ \rightarrow \ C_3H_2 \ + \ 5 \ H_2 \qquad (6)$$
$$C_2H_2 \ + \ 2 \ NH_3 \ \rightarrow \ 2 \ HCN \ + \ 3 \ H_2 \qquad (7)$$

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Still other reactions are possible, but they were not listed here since they do not greatly modify the results. In particular, the reactions (5) and (6) are symbolical for all dehydrogenation reactions of CH_4 that range from ethylene to carbon black.

TABLE XI

PYROLYSIS OF THE MIXTURE OF 80% H_2O, 12% CH_4, AND 8% NH_3

Equilibrium near 1500° K	Radicals Observed in the Comets		
68% H_2O	CH	[OI]	OH^+
14% H_2	–		–
8% CH_4	CH		CH^+
5% NH_3	NH	NH_2	–
2% CO	–		CO^+
1% CO_2	–		CO_2^+
1% N_2	–		N_2^+
1% HCN	CN		–
0.1% C_2H_2, $C_2H_4^*$	C_2		–
0.01% C_3H_2, C_3H_4, C_n^*	C_3		–

* See Note (18)

It is useful to state:

1) that each molecule listed (except H_2) is susceptible of being a parent molecule of a radical observed in the comas or in the tails;

2) that, reciprocally, no supplementary parent molecule seems necessary for explaining a radical observed in the comas or in the tails.

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Since we know definitely that equilibrium will not be reached, we made no effort to determine it with great accuracy. Nevertheless, in first approximation, at an equilibrium near 1500°K, the orders of magnitude shown in Table XI are obtained.

It is understood that the temperature of 1500°K has been adopted as a purely indicative value, that the listed reactions are already effective at lower temperatures, and that the increase in temperature merely displaces the equilibria toward the formation of greater quantities of new molecules.

4. Influence of Parameters on the Model

Another point to be discussed is the influence, on the results, of any variation in the numerical parameters adopted at the beginning, specifically the albedos and the radius of the nucleus. For distances of less than 3 or 4 a.u. from the sun, the numerical value of A_1 has practically no influence on the results. Conversely, for these distances, the production of gas is almost proportional to $1 - A_0$, such that, if A_0 is sufficiently elevated, the productions calculated for $A_0 = 0.1$ might be too high by a factor of 2 or even more.

If the radius R of the nucleus is different, since the theory of evaporation implies constant production rates at a given temperature per unit surface, it is obvious that the total production will be proportional to R^2. However, the concentrations and the mean free paths near the nucleus are independent of the radius R and only the height scale of the concentrations is proportional to this radius. For a given radius, the presence of pores does not change the efficient surface of evaporation, since these pores are filled with a gas that escapes by molecular flow, thus blocking an evaporation in depth. Only exceptionally large irregularities in the mean free path (several meters at least)

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might modify the efficient surface of evaporation for a given radius; however, in that case irregular forms of the nucleus rapidly are established, for which it will always be possible to define an effective radius corresponding to the effective surface of evaporation.

Finally, since a rapid rotation produces little change in the surface temperature distribution, it will hardly change the radiation according to Stefan's law and thus also will leave the overall production of the nucleus relatively untouched.

<div align="center">CONCLUSIONS</div>

A theory of vaporization, allowing for variations of the latent heat of evaporation with the temperature, has been applied to a cometary nucleus model, selected by making the simplest possible hypothesis as to its origin and constitution. The principal characteristic of this model is the great abundance of water molecules, whose presence has been confirmed in another paper of the author, based on quantitative considerations derived from observations of the OH radical in the comas (Delsemme, 1965).

The presence of snow or water ice implies the existence of hydrates of certain of the gases present, particularly CH_4 and NH_3.

If the molecule CH_4 is present in its cosmic abundance, a certain excess of free methane will exist in addition to the methane hydrate. This free methane might explain the particular behavior of "new" comets, as also confirmed by the heat of vaporization, calculated from a photometric curve of the Arend-Roland comet.

As soon as the free methane has disappeared, the existence of methane hydrate controls the abundance ratio of methane to water. Only an abundance of

<div align="center">30</div>

methane much lower than the assumed cosmic abundance of carbon could possibly change this result. The distribution of parent molecules, furnished by the nucleus, was calculated within the coma as a function of the heliocentric distance. The predicted concentrations in the coma are rather high, especially for water vapor, so that the appearance of a "chemical" coma could be expected where thermodynamic equilibrium is reached, enveloped by a "middle" coma where the thermodynamic equilibria, although not actually reached, are indicative of still possible chemical reactions. It was demonstrated that a thermosphere is formed, which rapidly penetrates into the mean coma when the comet approaches the sun. We compiled a list of the molecules produced by these chemical reactions at equilibrium and compared it to the radicals observed in the heads and tails; there seems to be a satisfactory one-to-one correspondence, which would a posteriori justify the hypotheses made as to the origin and constitution of the cometary nucleus.

<u>Notes</u>   /30

(1) It should be mentioned that the mathematical developments of the Soviet school have been possible because of the simplicity of approximation of the saturated vapor pressure of gases $P = AT^\beta$, used by Dobrovolsky (1953), an approximation that does facilitate the calculations but is much less accurate than the classical Clapeyron equation. This simplification of the mathematical approach results in a corresponding loss of physical significance of the formulas, particularly if an attempt is made to interpret photometric observations in terms of physical parameters. For example, the author verified that the value of $\beta = 13.1$, given for methane, is strictly applicable only near $100^\circ K$ since the value of β, for real methane, varies from 20 to 5 in the interval from 80°

to 160°.

Similarly, the value of β for water varies from 36 to 23 in the interval from 160° to 260° K. Conversely, the Clapeyron equation remains quite close to the real gases within the temperature range considered here, and the first noticeable deviations are produced for temperatures below 80° K.

(2) Everything passes as though the entire gaseous molecule, striking the interface between this molecule and its liquid (or solid) phase would always condense. Thus, a vapor becomes saturated on reaching a dynamic equilibrium in which the number of liquid or solid molecules evaporating per unit time is equal to the number of gaseous molecules striking the interface. This statement permits calculating the rate of evaporation of solids or liquids in vacuum. In fact, this rate is given by the number of gas molecules, calculated by the kinetic theory, that would strike the surface of evaporation under consideration if a saturated vapor instead of a vacuum were present.

Experimental data have shown that the theory is proved to within a coefficient quite close to unity (see Delsemme and Swings, 1951).

(3) In the theoretical formula of the rate of evaporation, the numerical /31 coefficient b_0 is obtained from the definitions and from the approximation adopted in the kinetic theory of gases. In fact, it is suggested to make alternate use of the mean-square velocity for pressures and of the mean velocity for fluxes; in the Maxwell approximation, these two velocities differ by $\left(\dfrac{8}{3\pi}\right)^{\frac{1}{2}}$, i.e., by about 8%. In practical application, this must in turn be multiplied by an experimental accommodation coefficient b_1 that adjusts the approximation to reality and that is generally close to 0.70, which is the value adopted here.

(4) The mean density in this case is 0.24, a value that is preferable to higher estimates in view of the fact that, since the force of gravity is of the

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order of 10^{-4} on the surface, the matter present there is much more likely to exist in the form of a light snow with numerous voids than in the form of ice. In addition, we will demonstrate that this snow generally is dry, since its melting point is hardly ever reached. The central pressure, due to gravity, in such a model is of the order of only 10^{-2} atm. These data, however, do not intervene much in the subsequent development.

(5) Our knowledge as to the relative abundance of O, C, and N is based mainly on observations of solar and stellar atmospheres.

In particular, the compilation by Suess and Urey (1958), so far as the abundance of O, C, and N is concerned, is based on a discussion by Aller (1958) who gave two series of values, one for the sun and the other for the mean of the young stars. These values, in our model, lead to 60% water, 6% NH_3, and 20% CH_4 (solar values) and, respectively, to 52% water, 18% NH_3, and 16% CH_4 (values of young stars). We preferred to use here the solar values as being more representative of matter in the solar system, despite the fact that this interpretation is open to discussion; however, it will be shown that the evaporation of free methane finally will approach both possibilities.

(6) As an indicative value, we are here limiting the temperature to a $\underline{/32}$ maximum of $150°K$ so as to establish the concept since, according to Note 4, the possible partial pressure of CH_4 is limited to 10^{-2} atm during formation of the hydrate whereas this hydrate can also exist above $0°C$ at a pressure of several atmospheres; on earth, the channels formed in moist methane, that become clogged at ambient temperature, are an eloquent proof of this.

Conversely, it is not known what takes place when approaching low temperatures. When the hydrates are very cold (several tens of $°K$), they might decompose, resulting in an empty crystalline lattice (see Table II). Miller (1961)

estimated that this might happen near $80^\circ K$. Because of the lack of data, we have neglected this eventuality since the hydrates anyhow reappear above this hypothetical temperature.

(7) The hydrates known in the laboratory follow more or less the empirical formula $CH_4 \cdot 6.9 H_2O$ since the crystalline lattice holes are not all filled at $300^\circ K$.

(8) For simplification, we wrote the hydrate of NH_3 in the form of NH_4OH; since NH_3 and H_2O are miscible in any proportion, to form ionic hydrates that all have a sufficiently high free energy of hydration (eutectic mixtures), it is probable that the equilibrium with the CH_4 hydrates tends in favor of a larger quantity of water associated with the NH_3. This particular question has not been studied further since its interest is only relative so far as the present discussion is concerned.

(9) Thus, the matter present must be visualized as a very dry snow since it has never been wetted. The probable forms of crystallization are, no doubt, fine needles interlinked by filamentary structures (Donn et al., 1963).

(10) This involves Whipple's convention (1950) so far as the albedo A_0 is concerned, although a larger albedo would be more plausible, if the outer layers of the nucleus were composed of all sorts of snow mixed with dust.   /33 In fact, the more or less contaminated terrestrial ices have albedos between 0.30 and 0.60 (Hubley, 1955) which would result in diminishing the rate of evaporation at a proportion that might reach a factor of 2. So far as the relative albedo A_1 at low-temperature radiation is concerned, its magnitude is of minor importance since the term σT^4 is small with respect to the heats of evaporation at significant distances.

(11) In the case of slow or zero rotation, a calculation of the tempera-

ture at various points of the nucleus, as a function of the zenith angle of the sun, demonstrates that the distribution is much more shallow than the well-known law in $(\cos \theta)^{1/4}$, which is due to a decrease in evaporation with increasing temperature. For example, starting with 70° K at the subsolar point, the temperature drops by 10° only for the point at which the sun is not more than 1.5° above the horizon. If a rotation of the nucleus were present, the phase lag introduced by the heating time (on rising) or cooling time (on setting) obviously would slightly modify the phenomena. This depends basically on the thickness of the surface layer penetrated by the solar flux, i.e., on the thermal insulation of the nucleus, which is high. The phase lag thus will be appreciable only for rapid rotations, and a surface temperature equipartition will be reached only for extremely rapid rotations.

(12) The depths of the various isotherms is decisive for the time required to establish equilibrium since the steady state depends on a selective sublimation up to these isotherms. To estimate these depths, the Whipple approximation on the heat transfer at the center of the nucleus indicates that this latter is highly insulating so that ΔT of the order of 100° K could be reached readily at much less than 10 m of depth. However, in our second model, a surface layer of 10 m depth contains 10^{14} gm of CH_4 which would have evaporated within two months at 3 a.u. and within one day at 0.6 a.u. This gives a general idea on the order of magnitude of the time necessary for obtaining such a quasi-steady equilibrium and suggests that this equilibrium, in general, would be realized /34 before the comet arrives at 3 a.u. on its approach to the sun.

(13) This reasoning demonstrates the error committed by Watson, Murray, and Brown (1963) in rejecting the presence of gas hydrates by stating: "they would be unstable on those bodies which are too small to retain their own atmo-

spheres". It is true that these hydrates are unstable, but they do not dissociate at infinite velocity; their dissociation rates are defined by the same laws as the velocity of sublimation of gas ices since they depend on a similar thermodynamic process, namely, a variation in free energy accompanying the change of state under consideration. On the other hand, even in the absence of an appreciable gravitational field, these rates of dissociation may be considerably decelerated by the establishment of a steady state with molecular flow of gases in the surface pores, as had been demonstrated previously.

(14) The existing mixed hydrate of argon and methane will stabilize the surface temperature for a brief instant, between the surface temperatures of methane and methane hydrate. This has been neglected only because of the fact that the cosmic abundance of argon corresponds to 2×10^{38} molecules in the model, such that it very little modifies the methane hydrate if cosmic abundance is assumed.

(15) In this preliminary analysis, we did not consider the contribution of other mixed hydrates. Miller (1961) treats only mixed hydrates of the clathrate type, which we need not consider in our model since the CH_4 hydrate is the only abundant substance here. Aside from the fact that it is not even certain that a mixed hydrate can be formed between CH_4 and one of the azeotropic forms of NH_3 hydrates, if such a mixed hydrate would exist then the various gases would be concentrated there in an inverse ratio of dissociation pressures of pure hydrates, which would mean - for example - that CH_4, at a temperature of $140^\circ K$, would participate only to within 0.1% of the NH_3, i.e., to $4 \times$ $\times 10^{13}$ gm, whereas 68×10^{16} gm would remain fixed in the pure hydrate of CH_4. Thus, its contribution again would be insignificant and would not at all change the steady state described below.

(16) It should be mentioned that, since H_2O and NH_3 are susceptible to combine in any proportion in the hydrate, $193^{\circ}K$ is a temperature above the melting point of any of the proportions comprised between 100% and 30% of NH_3. For less than 30% of NH_3 and more than 70% water, the fusion point rises rapidly toward the fusion point of water ice.

(17) This is true only when admitting an equipartition of energy in the gas undergoing evaporation, which constitutes a rather plausible hypothesis in view of the relatively short length of the mean free paths.

(18) The concentrations given for C_2 and C_3 do not correspond to the concentrations reached at equilibrium but to reaction times of 40 msec at atmospheric pressure (Delsemme, 1949), i.e., of the order of 40,000 sec for the pressures existing in the internal coma. However, these durations are exactly of the order of the residence time of the molecules in the internal coma, which justifies the given concentrations. It is known that the final equilibrium in this direction is lampblack (colloidal carbon) but that this is reached only at much longer reaction times for the temperature under consideration here (Delsemme, 1949).

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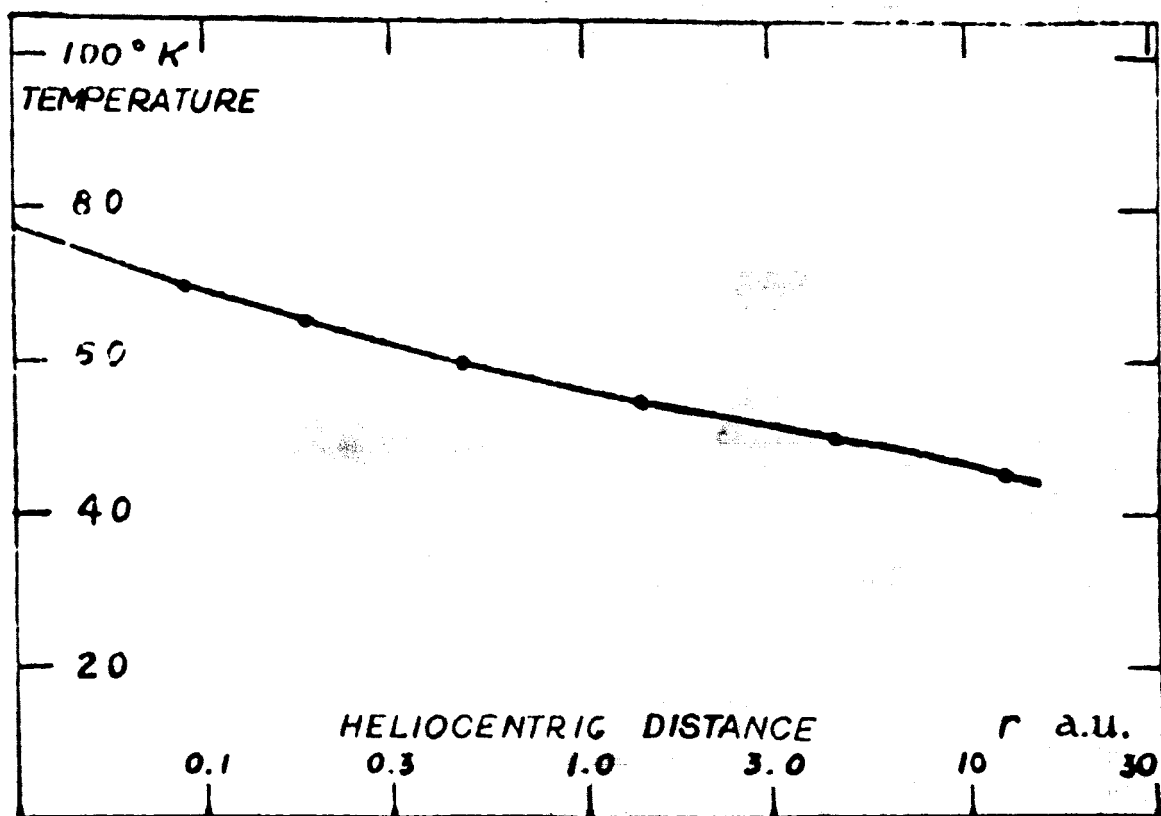
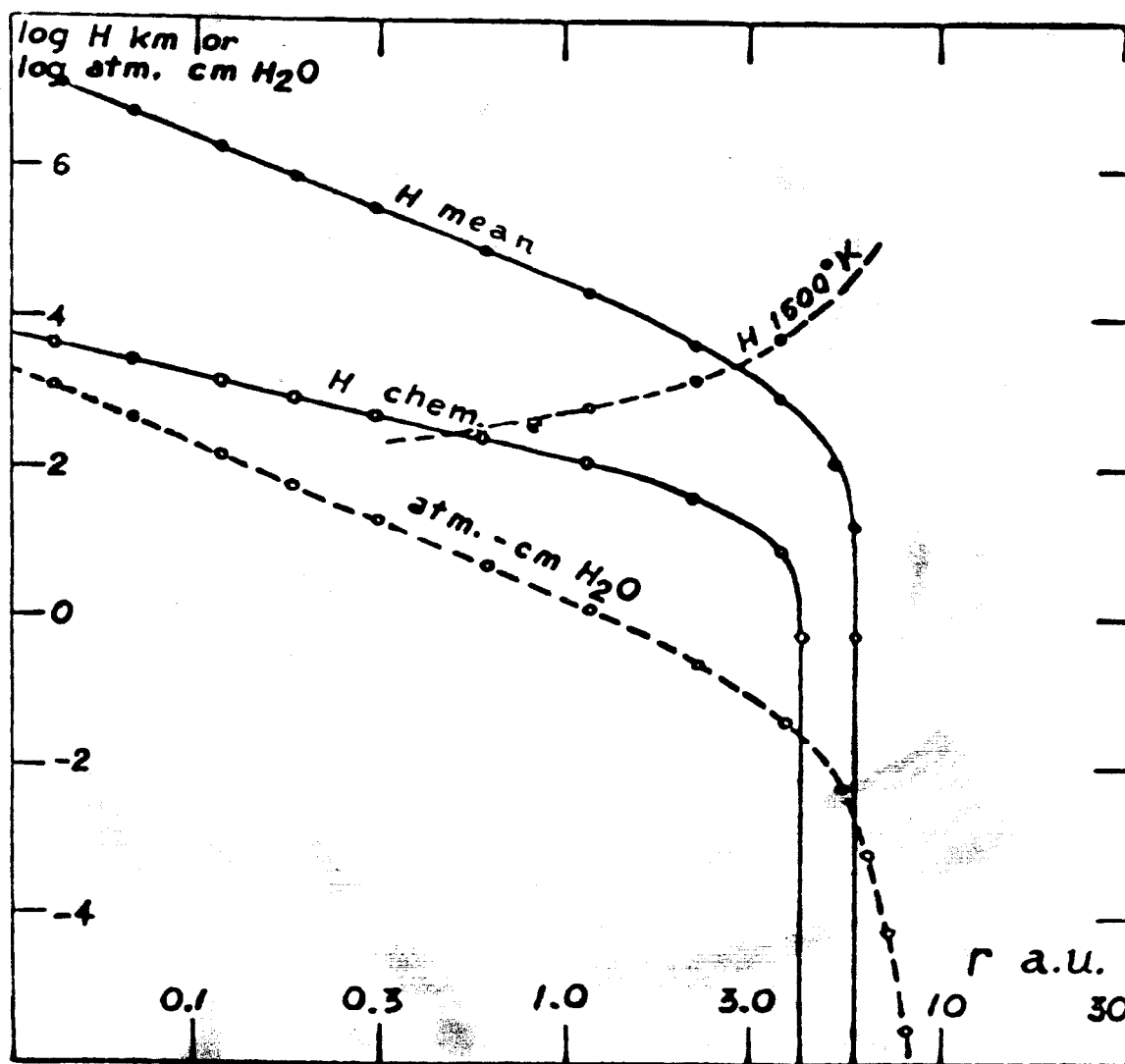Fig.1 Comet with Excess of CH₄
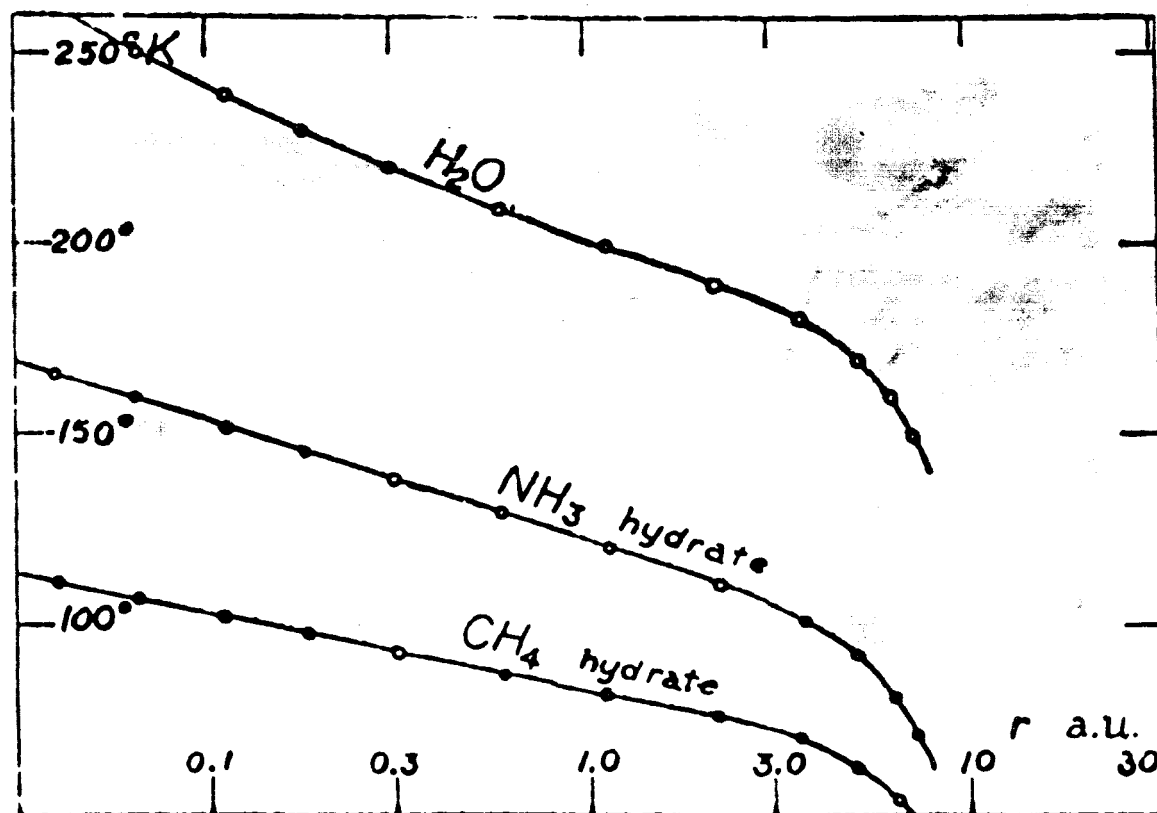
Fig.2 Comet without Excess of CH₄

Fig.3 Size of the Coma